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Ambient Monitoring of Pollutants Around Synfuel Plants

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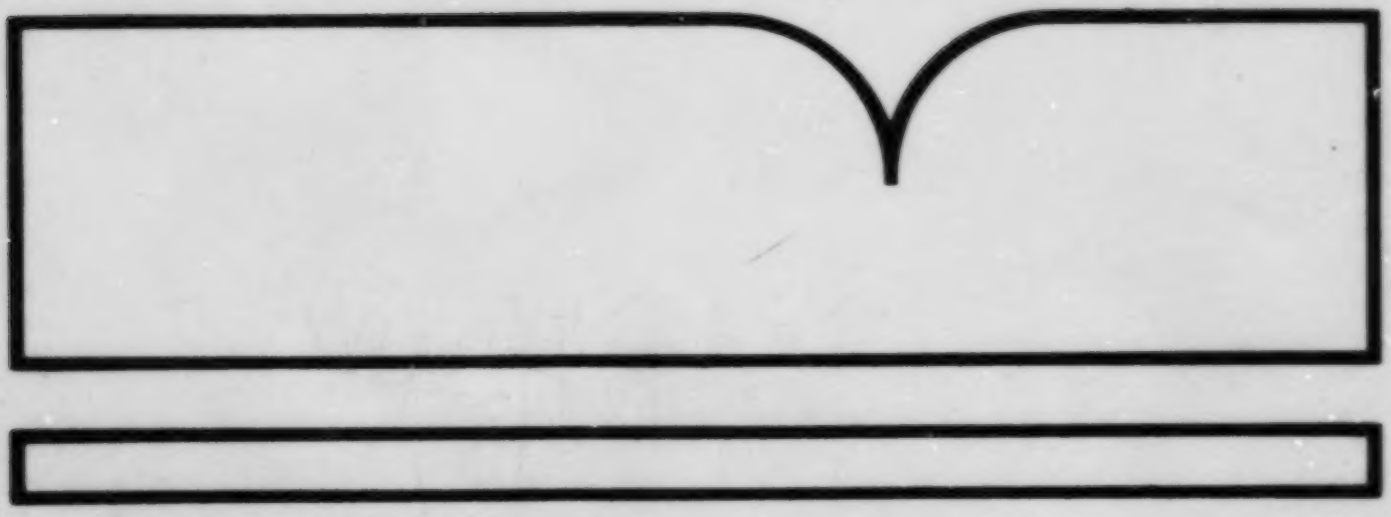

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The study is limited to evaluating the ambient monitoring plan of the EMP. Ambient monitoring we interpret as pertaining to the surveillance and measurement of pollutants that may emanate from the synfuel complex but are found outside the perimeter of the plant buildings and facilities. The perimeter usually will coincide with the fence or property lines of the complex. The ambient so-interpreted includes the airspace, and surface- and ground-waters, beyond, above and below the perimeter ("outside-the-fence") of the complex.

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AMBIENT MONITORING OF POLLUTANTS

AROUND SYNFUEL PLANTS

D.S. Golomb, S.A. Batterman and T.D. Rubin

Energy Laboratory Report No. MIT-EL 84-015

September 1984

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by

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September 1984

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SUMMARY

This study was undertaken to aid in the evaluation of Environmental Monitoring Plans (EMP) submitted to the U.S. Synfuel Corporation by prospective operators of large-scale synfuel plants who are applying for financial assistance. In accordance with the Energy Security Act of 1980, such applicants must provide an acceptable EMP in order to qualify for the assistance. The EMP is reviewed in consultation with the U.S. Environmental Protection Agency (EPA) and the Department of Energy. This study was sponsored by EPA to aid in their consultative role.

The study is limited to evaluating the ambient monitoring plan of the EMP. Ambient monitoring we interpret as pertaining to the surveillance and measurement of pollutants that may emanate from the synfuel complex but are found outside the perimeter of the plant buildings and facilities. The perimeter usually will coincide with the fence or property lines of the complex. The ambient so-interpreted includes the airspace, and surface- and ground-waters, beyond, above and below the perimeter ("outside-the-fence") of the complex.

Ambient air monitoring. The major emphasis of ambient air monitoring should be in the measurement of unregulated air pollutants such as volatile and condensible organic compounds, trace metals, and radionuclides for which emission standards are not yet defined, but are potentially hazardous to health and biota. As the identity, release rate and release height of the individual pollutants are not known a priori, tentative criteria are given for selecting the number and location of the monitors which can be modified as experience is gained on collected pollutant quantities and instrument sensitivities.

It is expected that most pollutants will emanate from low level (height) sources such as retorts, gasifier columns, sulfur recovery systems, liquid and solid waste disposal sites, and coal storage and handling systems. Ground-level pollutant concentrations will decline exponentially with distance because of horizontal and vertical diffusion. Multihour exposure may be necessary to collect a sufficient quantity of a pollutant for analysis. The meteorological factor having the greatest effect on the duration and frequency of sampling, and the location of the monitors, is the prevailing wind direction. Historical wind persistence analysis must be performed at each plant location to determine the wind sectors where the probability is greatest that multihour exposure will occur repeatedly over the monitoring period, say 1 year. It is proposed that monitors be placed in wind sectors where there is at least a 25% chance (100 days/year) that a collector be exposed to 6 or more hours per day (25%) of steady wind. If no single wind sector satisfies this requirement, monitors should be placed in several wind sectors such that at least 100 samples will have an exposure of 6 hours or more. The radial distance of the monitor should subtend an angle of 22.5 (one wind sector) with a cross section of the synfuel complex perpendicular to the monitor.

Ambient water monitoring.

The study involved an analysis of the behavior of organic effluents from a generic synthetic fuel plant in several representative environments. A generic approach was used because of the wide range of technologies used in synfuel development, and the variability of the aquatic environments which will receive their discharges. The approach was also necessary because there are no existing large-size synthetic fuel plants from which to obtain data. The analysis consisted of modeling the behavior of the effluents in generic environments. Specific compounds were chosen to represent broad classes of organic effluents. Also described are the schematizations of environmental processes used in the modeling.

Modeling results indicate that there is not a unique monitoring site or frequency for all compounds in all environments. The optimal monitoring site is determined mainly by effluent chemistry, and the optimal frequency by environmental characteristics. The results presented here will be useful once an effluent stream and environment are specified. Environmental monitoring plans may then be compared for the appropriateness of the planned monitoring sites and adequacy of sampling frequency.

1. INTRODUCTION

The Environmental Monitoring Plan Guidelines issued by the United States Synthetic Fuels Corporation (SFC) and published in the Federal Register (1983) identify three major categories of monitoring that wil be required in order to qualify for SFC financial assistance: 1. Source, 2. Health and Safety, and 3. Ambient Monitoring. The Environmental Monitoring Reference Manual for Synthetic Fuels Facilities published by EPA (1983) addresses two categories: 1. Source, and 2. Ambient Monitoring. However, both documents give rather limited guidelines to ambient monitoring. While source and process stream monitoring provides valuable information on the potential hazard to health and ecology from emissions and effluents, it is only ambient monitoring that can indicate the actual exposure, and hence risk, of the surrounding population and biota to these pollutants.

We interpret "ambient" monitoring to mean the measurement of pollutant concentrations in the airspace, surface- and ground-water, beyond, above and below the perimeter ("outside-the-fence") of the synfuel complex. The monitoring of possible health impacts on the surrounding population (by means of clinical and epidemiological studies), and monitoring of biological effects is not addressed here. Such monitoring is mentioned under "Other Monitoring" in the SFC Guidelines (Federal Register, 1983).

This study was undertaken (a) to aid the drafters of the EMP's to design effective and rational ambient monitoring procedures, and (b) to aid EPA and other official reviewers in evaluating the ambient monitoring portion of the EMP's.

2. AMBIENT AIR MONITORING

2.1 Introduction

This section concerns the monitoring in the vicinity of synfuel plants of unregulated air pollutants. The reasons for restricting the concern to unregulated air pollutants are twofold: (1) the regulated pollutants (e.g. SO_2, NO_x, TSP) are governed by New Source Performance Standards (NSPS). These standards limit their emissions at the source by applying the Best Available Control Technology (BACT). Once an NSPS review is completed, and assuming that emission standards will be met, ambient monitoring of the regulated pollutants would no longer be required.* (2) For large-scale synfuel plants, the major risk to the surrounding population and biota stems from the possible fugitive and accidental releases of unregulated and yet undetermined pollutants such as trace metals, radionuclides, polycyclic aromatic hydrocarbons (PAH), hydrogen sulfide and organic sulfides, cyanides, ammonia and organic amines and other volatile and condensible organic and inorganic compounds. Since many of these compounds are suspected toxigens, carcinogens and mutagens, their monitoring in the environment of the synfuel plant is of utmost importance.

We shall not review here the specific unregulated pollutants that may be emitted by synfuel plants, nor the methods and techniques for their

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*Except in Prevention of Significant Deterioration (PSD) cases. Ambient monitoring of regulated pollutants, however, would take place in Federal Class I Areas where the air quality deterioration is to be prevented, and not in the vicinity of the plant.

collection, characterization and analysis, as numerous references exist on that subject (e.g. EPA 1983; Keith, 1984). The emphasis here will be on the number and location of the required monitoring stations, and the duration and frequency of sampling.

2.2 Pollutant Dispersion

A monitor should be located where the probability is greatest that a pollutant will be detected, identified, and possibly quantified. Commonly, the steady state Gaussian dispersion equation is used to obtain the pollutant concentration at a ground location:

$$C(x) = Q[\pi\sigma_y(x)\sigma_z(x)u]^{-1} \exp\frac{1}{2}(H/\sigma_z)^2 \qquad (1)$$

Here C(x) is the concentration at the downwind distance x, Q is the source strength in units of mass per unit time, $\sigma_y(x)$ and $\sigma_z(x)$ are the horizontal and vertical standard deviations of the Gaussian plume profile at the downwind distance x, u is the wind speed, and H is the effective plume height. The plume height equals the release height plus the plume rise (for buoyant plumes). The σ'sare a function of the atmospheric stability category. In dispersion modeling, it is common practice to define 6 stability categories, from A (highly unstable) to F (highly stable),(Turner, 1970).

It is expected that most unregulated air pollutants from synfuel facilities will emanate from low height sources such as retorts, gasifier columns, sulfur recovery systems, liquid and solid waste disposal sites, coal piles and coal handling systems. Thus, H in Eq. (1) is usually

small, and the exponential factor close to unity. Maximum concentrations will occur close to the emission points; further downwind, the pollutant concentrations will decrease with distance due to the horizontal and vertical dispersion, and wind velocity. Ambient monitoring -- by definition -- is conducted in the surrounding environment, at some distance from the source(s). Therefore ambient monitors are not likely to be located at the point of maximum concentration. The amount of collected pollutant will be proportional to the concentration at the monitor location and the exposure time. The concentration is dependent on the dispersive quality of the atmosphere. Highly unstable conditions disperse the plume over a wider angle than neutral or stable conditions, causing the instantaneous concentrations to be smaller (see Eq. 1). The exposure time is dependent on the persistence of the wind transporting the pollutant to the monitor during a sampling period.

The proposed locations of the monitors are based on consideration of wind persistence only. A more sophisticated placement of the monitors should consider both wind persistence and atmospheric dispersion and will be the subject of further analysis.

2.3 Monitoring Frequency and Location

a. Frequency

The minimum time to collect a sample is dependent on emission rates, transformation rates, dispersion characteristics, distance to collector, instrument sensitivity, etc. As minute concentrations are expected, multihour exposure may be necessary. It is proposed to collect

pollutants over 24 hours, i.e. to change filters, substrates, absorption columns, bubblers, dosimeters, etc. every day at a constant hour, preferably at sunrise or sunset when meteorological conditions also tend to change.

b. Location

Azimuth. The greatest quantities of pollutant will be collected when winds blow steadily from the plant toward the monitor for a large fraction of the sampling time. We propose to locate the monitor in a sector where the winds persist for more than 6 hours per day (25% of the typical sampling period), for at least 100 days per year (about 27% of the samples). The hours need not be consecutive, but fall into the sampling period. A wind sector as defined by the National Climatic Center STAR register subtends an angle of 22.5° (16 wind sectors).

If no single wind sector experiences 100 events per year of 6+ hours duration, additional monitors would be required. However, for reasons of economy, the maximum number of monitors may be limited to three. If no three wind sectors experience 100+ events, exposures of 5+ hours, or slightly fewer events (e.g. 80-90) may be considered. A multiyear meteorological record is necessary for estimating wind persistences. The procedure is outlined in the examples given below.

Radial distance. The wind is defined to be steady if the direction stays within a STAR wind sector. Accordingly, we wish to locate the monitor(s) M_1 at the apex of the most persistent wind sector(s). The far side of the wind sector triangle is represented by the shortest cross

section d_i of the synfuel complex perpendicular to the monitor but encompassing all potential emission sources E_i (Figure 2.1). The radial distance to the monitor is $r_i = \frac{d_i}{2}/\tan(11.25°)$. As an example, for d_i = 1 km, r_i = 2.5 km.

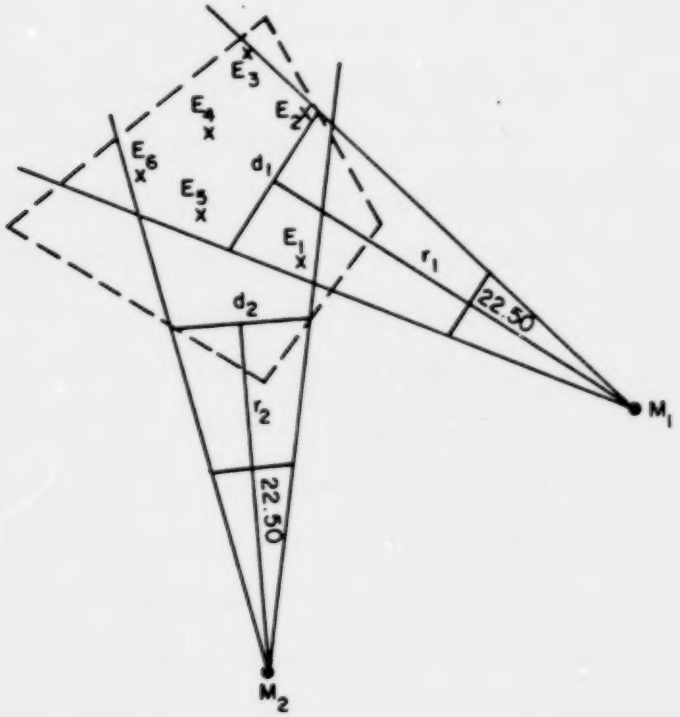


Fig. 2.1 Location of monitors around synfuel complex (dashed line).

2.4 Outlying emission sources

If the plant has strong emission sources at some distance from the main plant complex, separate monitors ought to be deployed for these outlying sources. For example, liquid effluents may be impounded at a distant site. Hazardous air pollutants may evaporate from the pond. At least one ambient monitoring station should be established in the most prevailing wind sector for sampling the evaporated stream.

2.5 Background monitoring

In general, it is advisable to monitor the background levels of the unregulated pollutants that may be conveyed to the synfuel complex from other industrial, urban and natural sources. This station could be set up in a wind sector that has the lowest probability of steady winds blowing from the plant, or alternatively, in the wind sector opposite the sector of greatest persistence. The latter alternative is probably superior because the background concentration can be obtained by subtraction of the upwind from the downwind levels.

2.6 Source monitoring

In order to understand source-receptor and precursor-product relationships, it is necessary to know the emission rates at the source(s) of the primary pollutants. This is referred to as source monitoring, and is recommended in the U.S. Synthetic Fuels Corporation Guidelines (FR, 1983). For improved source-receptor modeling and mass balance estimates, it is recommended that source monitoring at the major emission points (stacks, vents, flares) be continuous and simultaneous with the ambient monitoring.

2.7 Meteorological monitoring

For complete source-receptor modeling, it is essential to know all the meteorological factors that play a role in advection, dispersion and transformation of the emitted pollutants. Therefore, it is recommended that a standard meteorological station be continuously and simultaneously operated with the ambient monitoring. If another meteorological station

is nearby (say, within a 50 km radius of the plant), data from that station could be used if it provides representative meteorological information.

2.8 Examples

a. Daggett, CA

Table 2.1 is a wind direction persistence compilation for Daggett Airport, near Barstow CA, in the Mojave Desert, approximatley 190 km NE of Los Angeles. This example was chosen since the Cool Water Project, a major coal gasification combined cycle electric generating station, is being constructed nearby.

The wind data from the years 1955-64 were analyzed. Since only the annual wind roses were available, we used a statistical model (see Appendix 2.A) to obtain daily persistences. Table 2.1 lists the 5 wind sectors with maximum persistences. Column 1 is the number of hours per day that the wind blows in the same direction. The hours are not necessarily consecutive, e.g. a period of 3 hours in the morning and 3 in the evening would add up to 6 hours persistence on that day. The numbers in columns 2-6 are the cumulative events (days) per year that the wind direction persisted for the indicated hours or more. It is interesting to note that in the WNW and W sector, 24 hour persistences are possible, and these sectors have 167 and 142 events, respectively, of 6 to 24 hours persistence. It is likely that the two mountain ridges located to the north and south of Daggett channel the flow into the W-E direction.

Accordingly, the Cool Water complex would need only one ambient monitoring station in either the conjugate WNW or W sector, since an

Table 2.1 Cumulative number of events (days) per year with steady wind directions (hours per day) in the 5 most prevailing wind sectors at Daggett Airport, Barstow CA. Derived from average wind rose for the years 1955-64.

Persistence (hr/day)	Sector (direction from which wind blows)				
	WNW	W	WSW	NW	E
	Cumulative events per year				
1	320	312	247	232	175
2	281	267	166	147	84
3	247	228	112	93	40
4	217	195	76	59	19
5	190	167	51	38	9
6	167	142	35	24	4
7	147	122	23	15	2
8	129	104	16	10	1
9	113	89	11	6	
10	99	76	7	4	
11	87	65	5	2	
12	76	56	3	2	
13	67	47	2	1	
14	59	41	1	1	
15	52	35	1		
16	45	30	1		
17	40	25			
18	35	22			
19	31	19			
20	27	16			
21	24	14			
22	21	12			
23	18	10			
24	16	8			

adequate number of multihour exposures per year would be obtained in one sector. Note that the Table lists the sectors from which the winds blow. The monitors should be placed in the conjugate sector, eastward from the plant.

b. Chestnut Ridge, PA

Table 2.2 is a wind direction persistence compilation for Chestnut Ridge PA, approximately 60 km east of Pittsburgh. This is a hilly, rural, inland site with rather persistent winds due to channeling by two parallel ridges. The most persistent winds are from the west, the least persistent ones from the north. In this case too, a single monitoring station in the conjugate WNW sector would record more than 100 days of 6 or more hours persistence. A second station in the conjugate W or WSW sector would increase greatly the probability of obtaining an adequate number of multihour exposures.

c. Grand Junction, CO

Table 2.3 pertains to the wind statistics at Grand Junction CO, located on an elevated plateau with relatively frequent unstable conditions and variable winds. Here none of the sectors have very stable winds. The maximum persistence is 15 hours in sector SE. Nevertheless, a single monitor placed in the conjugate SE sector would experience 128 events per year of 6+ hours duration, but it would be prudent to set up another station in the conjugate ESE sector.

Table 2.2 Cumulative wind persistence at Chestnut Ridge, PA, for 1977-79

Persistence (hr/day)	Sector (direction from which wind blows)				
	SSE	WNW	W	NW	WSW
	Cumulative events per year				
1	142	245	235	207	235
2	109	205	194	165	194
3	92	171	164	138	164
4	78	141	142	119	142
5	64	117	118	99	118
6	51	102	97	83	97
7	44	84	82	66	82
8	32	71	68	56	68
9	29	56	55	47	55
10	23	46	45	41	45
11	18	37	37	35	37
12	15	30	28	30	28
13	11	23	19	23	19
14	9	20	16	19	16
15	7	16	10	15	10
16	5	13	8	14	8
17	5	9	6	10	6
18	4	8	6	6	6
19	2	7	5	5	5
20	1	5	4	4	4
21		2	3	3	3
22		1	2	3	2
23		1	1	2	1
24			1	1	1

Table 2.3. Cumulative wind persistences at Grand Junction, CO, 1977-79.

Persistence (hr/day)	Sector (direction from which wind blows)				
	E	ESE	SE	SSE	NNW
	Cumulative events per year				
1	274	328	358	277	290
2	144	236	308	178	180
3	65	166	264	103	98
4	28	98	217	61	52
5	12	60	167	34	24
6	5	33	128	19	13
7	1	17	83	11	8
8		9	50	5	4
9		2	29	2	2
10			19	1	1
11			6		
12			2		
13			1		
14			1		
15			1		

2.9 Conclusions

Ambient monitoring for air pollutants at synfuel plants is presumed to pertain to unregulated pollutants (e.g. volatile and condensible organic compounds), for which there are not yet promulgated source emission standards. Since only minute quantities are expected in the ambient ("outside-the-fence") of a plant, multihour exposures will be necessary to analyze the collected samples. Consequently, monitors should be placed in prevailing wind sectors. It is proposed to collect at least one hundred samples per year that have been exposed to 6 or more hours of steady wind per day. The distance from the plant to the monitors should be such that the monitor subtend a 22.5° angle (one wind sector) with a cross section of the plant perpendicular to the monitor.

2.A Appendix

As only the average annual wind rose was available for Daggett airport, CA, a statistical model was developed to derive daily persistences. The average annual frequency of daily wind direction persistence was calculated at two locations (Grand Junction, CO, and Chestnut Ridge, PA) using three years of surface observations at each site. The persistence was calculated for 16 sectors at each site and corrected for missing data. The cumulative persistence of each sector was observed to fit very closely an exponential model. Coefficients for the exponential distribution were determined by linear regression. The 32 coefficients were then regressed against the annual probability of each wind sector. Both sites showed good agreement with this model. This two stage procedure permits an estimate of sector persistence using only the annual probability of the wind sector.

2.R References to Section 2

Federal Register (1983), "Final Environmental Monitoring Plan Guidelines," 48: 46676.

Environmental Protection Agency (1983), "Environmental Monitoring Reference Manual for Synthetic Fuels Facilities," EPA-600/8-83-027, Washington, D.C. 20460, also available from NTIS.

L. W. Keith, ed., 1984, "Identification and Analysis of Organic Pollutants in Air," Butterworth Publishers, 80 Montvale Ave., Stoneham, MA 02180.

D. B. Turner (1970), "Workbook of Atmospheric Dispersion Estimates," Environmental Protection Agency, Research Triangle Park, N.C. 27711.

3. SURFACE WATER MONITORING

3.1 Introduction

Monitoring is intended to protect the public and the environment in general. It is meant to avert problems associated with public health, productivity of land and water bodies, and environmental integrity. All of these may be harmed by the presence of excessive amounts of toxic chemicals in drinking and irrigation water, lakes, river and groundwaters. Monitoring effluents from mines which supply the feedstock for synfuels, and occupational safety and health monitoring within the synfuel plant complex are not discussed here.

The environmental problems are of two types. One is the chronic problem of a slow, more or less steady discharge of contaminants from normal plant operations. Accumulation is most likely in sediments and biota, and environmental monitoring should be performed at specific sites to be most effective. Predictive modeling of contaminant distribution is most useful in identifying these sites. The difficulty in detecting this type of contamination arises from both the slow changes in concentration at a given site and also the large area over which these sites may be located.

The other type of contamination is the sudden, "spill-type" release of a pollutant, creating a more acute problem than the slow steady discharge. These releases could be the result of leaks, spills and cleaning operations (e.g. backflushes of plant equipment), or extreme environmental events such as floods and heavy rainfall (causing excessive runoff from feedstock or waste piles). This type of release can be difficult to detect due to the low frequency and unpredictable occurrence.

These problems were approached by creating a generic synthetic fuel plant which combines the available data of experimental plants, and simulates the effects of its discharges on representative environments as may be encountered in the future. The discharges were characterized by selecting specific compounds representative of broad classes of organic effluents. Their behavior in typical environments was modeled using readily available chemical data, chemical estimation techniques, and various schematizations of environmental processes.

Modeling results include prediction of contaminant concentration in sediments and the water column of different environments, as well as an index of the rate of decrease of the concentration in each location after loading ceases. A sensitivity analysis was performed to determine which chemical and environmental factors exert the most influence on model results. After summarizing model results, generalizations are made about the factors which are most important in determining sampling site and frequencies.

3.2 Modeling

Three generic aqueous media were selected as likely recipients of synfuel liquid discharges:

1. A western river such as the Colorado River near Rifle, CO, an area expected to have significant oil shale development.
2. An eastern river such as the Green River near Munfordville, KY, located in a region with substantial potential for coal development.
3. A typical eutrophic lake.

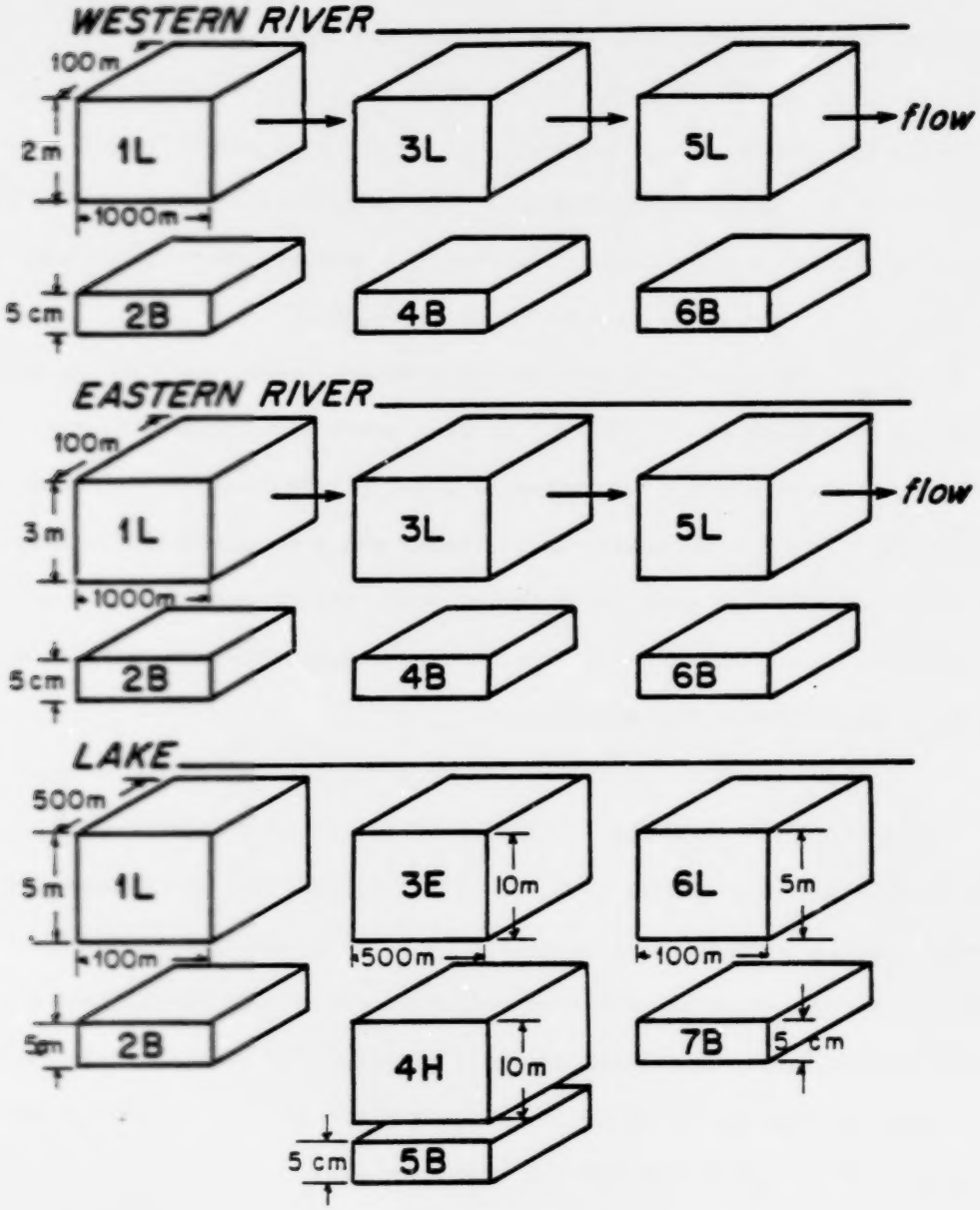
Each medium is described in terms of homogeneous compartments, namely littoral, benthic, hypolimnion and epilimnion (Fig. 3.1). The classification serves as a control in order to determine which environmental processes are active, e.g. there is no volatility calculation for benthic compartments. The compartments are connected via advective and dispersive terms. Internally, however, each compartment is homogeneous in that it is assumed to be fully mixed.

The EXAMS (EXposure Analysis Modeling System) model was used in these calculations (Burns et al, 1981). It is a predictive, deterministic model. All processes are described as a set of simultaneous differential equations. This set of equations is linked via a conservation of mass equation, whereby the rate of change of pollutant concentration in any compartment is a function of inflow loadings, advective and dispersive exports, and chemical degradation.

The set of equations is solved via standard discretization of time and space dependent functions. Spatial discretization (necessary for computing dispersion rates) is achieved by breaking the environment into compartments. Temporal discretization is achieved internally where time varying forcing functions (such as pollutant concentrations in second order chemical rate equations) are held constant for short periods, the equations are solved for that time step, and the forcing functions are then updated to new values for the next time step.

The model assumes that the presence of a compound does not change the properties of the environment. For example, absorbance of light by a pollutant does not change the light attenuation rate in the water column,

Figure 3.1 Compartments in representative environments.



L = littoral, B = benthic, E = epilimnion, H = hypolimnion

bacterial populations are neither poisoned nor encouraged to grow by the presence of the compound.

The chemical compounds modeled here are listed in Table 3.1. The list includes acidic, basic and neutral fractions of the total effluent load; straight chain and ring compounds, both sulfur and nitrogen heterocycles, a polycyclic aromatic hydrocarbon, and a carboxylic acid. The list includes all of the compounds in Stuermer's (1982) list of "indicator compounds" for coal gasification effluents, and alkylpyridines, which Riley et al (1981) suggested for use as "fingerprints" of synthetic fuel effuents. Benzo-a-pyrene is included in the list even though it does not appear in any of the analyses listed. It is expected to be present in air emissions; in liquid effluents the presence of benzo-a-pyrene is less likely. Nevertheless, its monitoring is warranted because it is a suspected carcinogen.

Some pertinent chemico/physical input parameters for the model are also listed in Table 3.1. Where data was unavailable, default values suggested by Burns et al (1981) were used. The selection of parameters is described in detail by Rubin (1983).

3.3 Modeling Results

The important results for all the selected compounds are summarized in Table 3.2. The purification time index shows the environmental response after the effluent load ceases. This index represents the time necessary for the aqueous concentrations in the water column or the sediment concentration in the benthic compartment to

Table 3.1 Representative Effluents and Chemical Data

Compound	Molec. Weight	Solubility (mg/l)	Vapor Pres. (atm)	Henry's Law Constant ($atm\text{-}m^3/mol$)	K_{ow}^{*}	k_{bio}^{**} ($ml\ cell^{-1}hr^{-1}$)	k_{ox}^{***} ($\mu mol^{-1}hr^{-1}$)	quantum yield dim'less)
Phenol	94.11	8.3E4[8]	6.5E-4[c]	4E-7[e]	29.5[f]	-	-	0.016[d]
Cresol	108.1	1800[a]	0.108[a]	-	85[f]	5.2E-7[a]	12.57[a]	0.079[a]
Heptanoic Acid	130.2	2.4E3[b]	-	4.7E-5[e]	199[f]	-	-	-
Xylene	106.2	100[8]	0.0104[e]	6E-3[e]	1410[f]	-	-	0.016[d]
Naphthalene	128.2	31.4[h]	1.1E-4[e]	4.2E-4[e]	2340[f]	-	-	0.016[d]
Benzo-a-pyrene	252.3	1.2E-3[a]	5E-9[a]	-	2.4E6[a]	0.0[a]	14.54[a]	7.2E-4[a]
Aniline	93.12	35[b]	0.67[c]	-	7.9[f]	-	-	0.016[d]
Picoline	93.12	1E6[b]	-	6.9E-6[e]	16.6[f]	-	-	0.016[d]
Quinoline	129.1	6110[a]	9.1E-3[a]	-	108[f]	3.1E-6[a]	12.57[a]	3.3E-4[a]

*K_{ow} = partition coeff. between octanol/water

**k_{bio} = biodegradation rate

***k_{ox} = oxidation rate

Sources:

a. Smith el al, 1978
b. Merck, 1976
c. Boublik et al, 1973
d. value averaged from Smith et al, 1978
e. Hine and Mookerjee, 1975
f. Hansch and Leo, 1979
g. Seidell, 1941
h. Yalkowsky and Valvani, 1980

Table 3.2 Predicted contaminant concentrations and purification times in generic environments.

Compound	Environment[1]	Concentration (ppb)		Purification Time Index	
		Water	Sediment	Water	Sediment
Phenol	W	500	60	2 hr	12+ hr
	E	500	100	2 hr	12+ hr
	L	200	6	182 day	312 day
Cresol	W	900	4000	2 hr	12+ hr
	E	900	3500	2 hr	12+ hr
	L	10	10	91 hr	156+ hr
Heptanoic Acid	W	20	5	2 hr	12+ hr
	E	20	30	2 hr	33+ hr
	L	60	30	60 day	60+ day
Xylene	W	0.5	0.5	2 hr	12+ hr
	E	0.5	7	2 hr	12+ hr
	L	10	200	16 day	24+ day
Naphthalene	W	2	3	2 hr	12+ hr
	E	2	40	2 hr	12+ hr
	L	20	400	11 day	12+ day
Benzo-a-pyrene	W	0.5	100	2 hr	24+ hr
	E	6	4700	18 day	36+ day
	L	0.1	8000	100 mo	100 mo
Aniline	W	4	0.5	2 hr	12+ hr
	E	4	0.7	2 hr	12+ hr
	L	200	1	228 day	228+ day
Picoline	W	4	0.5	2 hr	12+ hr
	E	4	0.7	2 hr	12+ hr
	L	100	2	168 day	168+ day
Quinoline	W	1	6	2 hr	12+ hr
	E	1	3	2 hr	12+ hr
	L	5	3	18 hr	36+ hr

1. W = western river E = eastern river L = lake

decrease to one-fourth of their steady-state (equilibrium) values. Assuming purification to be a first order process, the time corresponds to a passage of two halflives. This index is useful as a guide in selecting a monitoring frequency.

In some cases, the model results included an adjustment to pollutant loadings. This is because the model requires pollutant concentrations which are very low (often well below the solubility limit of the compound in water), in order for certain assumptions, such as linearity of sorption isotherms, to be valid. Furthermore, except for phenol, adjustment was necessary only in the lake environment, which has a much lower streamflow rate, and thus less dilution, than the river environments.

The adjustments do not substantially decrease the utility of the modeling, nor do they imply that the environment is incapable of accepting larger loads. Rather, they keep all values within the safe operating limits of the assumptions necessary in a large model which integrates many processes. The adjustments could have been obviated by increasing the size and flow rates of the lake, but this would defeat the purpose of investigating the impacts of these effluents on smaller water bodies with low flow rates. It is extremely unlikely that all of the aqueous effluents from a synthetic fuel plant would be discharged into a lake of the size modeled here. The modeling is intended for situations such as those in Lake McKellar near Memphis (Memphis Gas, Light and Water, 1982) or Pungo Lake in North Carolina (Peat Methanol Associates, 1983), where a relatively small lake may receive a portion of the discharges from a synthetic fuel plant.

3.4. Monitoring Sites and Frequency

The choice of monitoring site depends on several factors. One is the location of highest concentration; there pollutants are easiest to measure and probably the most reliable results will be obtained. Another factor is the sensitivity of the local concentration to changes in the pollutant load, i.e. some sites may reflect changes of discharge rates faster and more reliably than others. The last major factor is related to the purification time: assuming that there is a location with high concentrations and responsive to larger environmental changes, does it have a "memory" of such changes, or would monitoring have to be essentially continuous at this location?

Not all of these factors can be optimized simultaneously. In the absence of spills, high concentrations usually take a long time to develop. These sites therefore do not respond rapidly to changes in the environment as a whole. Conversely, a site which has rapid environmental response is unlikely to preserve a record of the responses.

Hydrophilic compounds such as phenol, aniline and picoline have higher concentrations in the water column than in the sediments regardless of the environment. In the lake environment, the difference in aqueous and sediment concentrations is two orders of magnitude, but in rivers, the difference is always less than an order of magnitude, and is not conclusive.

In contrast, the neutral compounds naphthalene, xylene, and benzo-a-pyrene, always have sediment concentrations greater than or equal to those in the water column. Again, in the river environments this generalization becomes weaker. For example, predicted concentrations of xylene in the sediment and water of the western river are identical.

The remaining compounds may have concentration maxima in either water or sediment depending on the environment. The choice of sediment vs. water column sampling depends mainly on the chemistry of the compound. The location of maximum concentration tends to be constant for various classes of compounds (e.g. hydrophilic, hydrophobic), and independent of environment. Neither water column nor sediment sampling will always give the best results for monitoring all compounds.

Similarly, there is no optimal monitoring frequency for all compounds in all environments. However, patterns of behavior are discernible. For all compounds, aqueous concentrations in the water column of rivers passed two halflives within about two hours after the pollutant release stopped. Concentrations of all compounds (except benzo-a-pyrene and heptanoic acid) in river sediments passed two halflives in 12+ hours. Purification time indices in the lake environment had a much wider range, from hours for aqueous quinoline to years for benzo-a-pyrene. The reason that rivers purify faster than the lake, and the water column purifies faster than sediments is that advection is always the fastest mechanism for purification. Where significant advection occurs, purification is maximized. Purification time indices depend mainly on the environment, and are relatively independent of a compound's chemistry. This indicates the need for detailed environmental data when designing and evaluating environmental monitoring plans.

The usefulness of the purification time index for some compounds in sediments is somewhat diminished due to the structure of the EXAMS model. In calculating system response, the program reports concentrations for twelve time steps after load cessation. The length of

the time steps is determined by the fastest purification time scale. In rivers, the time increment is usually one hour due to the rapid purification of the water column by advection. However, when this same time increment is applied to sediments, the two half-lives point is never reached in a twelve-hour period. Thus, a 12+ hour purification index could actually mean a very small concentration decrease in this time period.

3.5 Conclusions

Monitoring should be performed at sites where relatively high pollutant concentrations will be found, and are sensitive to loading rate changes. However, different compounds may have concentration maxima at different sites, therefore a single site may not be adequate for all compounds.

The site (sediment vs. water column) depends mainly on the particular compound to be monitored, especially its hydrophobicity. The intuitive guide of sampling hydrophobic compounds in sediments and hydrophilic compounds in the water column should be followed; this is verified by the modeling results. Phenol, aniline, and picoline typify hydrophilic compounds, while benzo-a-pyrene typifies a strongly hydrophobic compound. Heptanoic acid and quinoline are the most equivocal, and the critical K_{ow} for separating hydrophobic from hydrophilic compounds is in the order of 10^2. (K_{ow} is the single most important chemical parameter for determining where to sample, though essentially all parameters exert some control on sampling site.) The expected pollutant

concentrations can only be obtained by performing detailed site specific modeling based on a particular effluent rate in a specific environment.

Sampling frequency is mainly determined by the environment. Water column samples from rivers are of limited value in detecting spill-type releases unless collected at intervals of less than two hours. This also applies to composite samples, i.e., components of the composite must be collected at least every two hours. If actual analysis is to be performed only once a week, dilution problems can easily arise, since a spill which is present during only one 2-hour period will be diluted 83 times in the weekly composite. In most cases, weekly samples of a lake's water column will be effective in detecting spill-type releases. Chronic pollution will be best revealed in sediments. Long term changes of pollutant concentrations in sediments can be detected by samples taken at intervals of at least a week, and possibly a month or more. The critical frequency for any particular situation (including collection and analysis of composite samples) can only be determined through detailed modeling, and will be dependent on environmental data, especially such hydrologic variables as gross flow rate, direction of groundwater flows, etc.

4. GROUNDWATER MONITORING

In the absence of detailed knowledge of the groundwater at a given synfuel site, it is suggested that groundwater monitoring follow the practices set forth for the Resource Conservation and Recovery Act (RCRA). For RCRA groundwater monitoring, the standard practice is to put one monitoring well upgradient of the facility and three wells downgradient. The three downgradient wells are to be oriented roughly in a line perpendicular to the direction of groundwater flow. All wells are placed at or near the edge of the facility.

The frequency of sampling is much lower in groundwater than in surface water. Groundwater moves relatively slowly, usually in the range of meters per day at most. Thus, sampling four times per year is usually adequate to detect contamination problems.

If there are multiple aquifers underneath a site, then each aquifer which is exposed to contamination should be monitored. In most cases, this would include a very shallow phreatic aquifer in addition to the uppermost confined aquifer. If the aquifers are thick, i.e., more than a few tens of feet, they should have one monitoring well screened at the top of the aquifer and one at the bottom. This arrangement will help assure good sampling coverage since some pollutant plumes tend to rise and others to sink in groundwater.

These suggestions are seen as a minimal degree of sampling coverage. Most synfuel plants will be quite large, and should have more than three downgradient wells. Additionally, as more information on the geohydrology of a given site is obtained, the monitoring plan may be adapted to reflect local conditions. For example, if a site is underlain

by channel-fill deposits (sands and gravels), there may be avenues for rapid contaminant migration along old drainages. These areas would receive special attention in the form of more monitoring wells and increased sampling frequency. However, due to the extremely wide range of potential groundwater environments, a generic monitoring plan is of limited value.

Well construction and sampling methods have been described in detail in recent publications, e.g., Marion et al (1980); Berg (1982).

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